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(54) Title: ROOF SHEETING AND FLASHING ELASTOMERIC COMPOSITION (57) Abstract Ambient temperature curable rubber roofing or sheeting compositions based on ethylene/propylene/diene terpolymer or butyl rubbers cured with the essential curatives of alkylthiourea/sulfur. Preferably, thiazole or thiuram and dithiocarbamate type accelerators may also be added.		

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5 **ROOF SHEETING AND FLASHING**
 ELASTOMERIC COMPOSITION

BACKGROUND OF THE INVENTION

 The instant invention relates to an elastomeric
10 composition selected from the group consisting of ethyl-
 ene-propylene-non-conjugated diene terpolymer (EPDM),
 isobutylene-conjugated diene copolymer (butyl rubber) and
 mixtures of the terpolymer and copolymer. More particu-
 larly, the instant invention is directed to an elasto-
15 meric composition selected from the group consisting of
 ethylene-propylene-non-conjugated diene terpolymer,
 isobutylene-conjugated diene copolymer and mixtures of
 the terpolymer and copolymer which may be applied to a
 roof as roofing sheets or flashing members which, upon
20 exposure to ambient influences, have the ability to
 cross-linked.

BACKGROUND OF THE PRIOR ART

 Elastomeric ethylene-propylene-non-conjugated diene
 terpolymer (EPDM) and isobutylene-conjugated diene
25 copolymer (butyl rubber) compositions are well known in
 the art. The use of EPDM and butyl rubber compositions
 as the material of construction of roof sheeting is also
 known in the art. Such sheeting provided in the cured or
 cross-linked state provide excellent materials for use on
30 a roof in those applications where flat material is

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acceptable for disposition on equally flat or moderately contoured roofing structures. However, when the cross-linked EPDM or butyl rubber sheeting of the prior art is disposed on intricately contoured surfaces of a roof, such as parapet, chimney, ventilator sections and the like, the flat cross-linked sheeting of the prior art is not acceptable. That is, cross-linked EPDM or butyl rubber lacks the formability to successfully and permanently follow, cover and retain irregular shaped contours.

10 Roofing material used to follow irregular contours is known as flashing. Cross-linked EPDM or butyl rubber roof sheeting is not normally used as flashing because gaps readily develop around the contours between the sheeting sections of the roof, and those other portions
15 of the roof in which the EPDM or butyl rubber is employed as flashing.

Whereas cross-linked EPDM or butyl rubber sheeting have each established excellent reputations as effective barriers to roof leaks on the surfaces upon which they are applied, still, this protection has not been available to those portions of the roof which are characterized by their irregular shape. Thus, the excellent protection afforded by EPDM or butyl rubber compositions has not been available as flashing. This results in the
20 inability to protect those sections of the roof characterized by irregular shape against leakage. The utilization of EPDM or butyl rubber roof sheeting, a most
25 effective long term protector against water leakage, is

seriously compromised by this defect in cured EPDM and butyl rubber.

It is the object of this invention to prepare improved accelerator-vulcanizer blends for use in ethylene-propylene-non-conjugated diene terpolymer (EPDM) roof sheeting which would allow EPDM sheet to cure in situ during roof service providing properties similar to conventional vulcanized roof membrane.

The use of EPDM compositions as the material of construction of roof sheeting is well known in the art. Also, EPDM compositions containing accelerator-vulcanizer blends for in situ curing of roof sheeting and flashing is known, e.g., U.S. patent 4,461,875 (A.E. Crepeau).

U.S. Patent 3,531,444 describes a vulcanizable composition comprising sulfur, zinc oxide, a sulfur vulcanizable hydrocarbon elastomer and a vulcanization accelerator composition comprising a combination of a bis(morpholiniothiocarbonyl) sulfide and thiuramsulfide or a metal dithiocarbamate.

U.S. Patent 3,644,304 is directed to a vulcanizable composition containing a diene modified ethylene--propylene elastomer, copper 2-mercaptobenzothiazole and a thiuram sulfide or a metal dithiocarbamate.

The preparation of EPDM polymers having grafted thereon vulcanization accelerators and polymer blends with highly unsaturated diene rubbers that are cured using sulfur are disclosed in U.S. Patent 3,897,405.

Another reference of interest is U.S. Patent 4,012,332 which discloses an accelerator composition for the vulcanization of diene elastomers, comprising a benzothiazole sulfenamide, a thiuram sulfide and copper 2-mercaptobenzothiazole.

The lack of elasticity of uncured EPDM in addition to its favorable characteristics of excellent weatherability, low temperature flexibility and resistance to direct sunlight lends itself for use as roof flashing.

Once the uncured EPDM roof sheeting and flashing are installed, it is desired that the ambient cure takes place as soon as possible so as to develop desirable physical properties similar to vulcanized roof membrane.

Surprisingly, it has been found that certain dialkylthioureas as the primary accelerator in curative triblends show faster self-cure at ambient temperature than known blends containing dipentaethylenethiuram hexasulfide (DPTH) as the primary accelerator, as taught in U.S. 4,461,875, and the related patents, U.S. 4,514,442 and U.S. 4,666,785.

In accordance with the instant invention, a composition is provided which comprises 100 parts of ethylene--propylene-non-conjugated diene terpolymer (EPDM); 0.1 to 3.0 parts of dialkylthiourea; and 0.4 to 5.0 parts of one or more sulfur donor curatives.

DETAILED DESCRIPTION OF THE INVENTION

In an embodiment of this invention a roofing composition is provided in which the curing composition of

this invention is incorporated. The roofing composition may be in the form of sheets of the desired dimensions, usually formed by calendering or extruding the sheet, then cutting the sheet to proper size and shape. The
5 sheets may be cut for use as roof sheeting or flashing members.

When used as a roof covering, the composition of this invention may cover any roofing base material, such as wood, composition board, concrete, brick or metal. In
10 many applications, insulating or vapor barrier layers may be first placed over the roof bottom prior to the disposition of the composition of this invention. It is emphasized, however, that such layers are not essential to the carrying out of this invention.

15 Another aspect of this invention is a method of protecting roofs from water leaks by disposition thereupon of the composition of this invention.

In another preferred embodiment the composition of this invention is employed as a water liner. In this
20 application sheets of the composition are employed as a reservoir liner, a pond liner and the like.

The composition of this invention comprises an elastomer selected from the group consisting of ethylene-- propylene-non-conjugated terpolymer (EPDM),
25 isobutylene-conjugated diene copolymer (butyl rubber) and a mixture of EPDM and/or butyl rubber. These EPDM and butyl rubbers generally have iodine numbers below 100. Optionally, a smaller proportion (less than 40%) of

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sulfur vulcanizable natural or synthetic elastomers having iodine numbers above 100 (i.e. SBR, BR, IR, NBR, MR) present with a critical compound of the thiourea class of accelerators. The alkylthio- ureas are the general type with the following materials being preferred compounds, N,N'-diethyl-thiourea, ethylene thiourea, dimethylethylthiourea, trimethylthiourea, tetraalkylthiourea. Most preferred are ethylene thiourea and N,N'-diethylthiourea.

10 The second critical cure compound is sulfur, preferably in elemental form such as the commonly used rhombic crystalline form called rubber makers' sulfur or spider sulfur. The third critical cure component is a cure accelerator of one of the following classes:

- 15 1. Thiazoles, representative materials are benzothiazyl disulfide, 2-mercaptobenzo-thiazole.
2. Thiuram monosulfides, thiuram disulfides. Among the thiuram mono- and disulfides, are included lower-alkyl, monocyclic ar (lower-alkyl), aryl and cyclic alkylene thiuram sulfides representative materials include:

25 Tetramethylthiuram disulfide,
Tetramethylthiuram monosulfide,
Tetraethylthiuram disulfide,
Tetrabutylthiuram monosulfide,

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Diisopropylthiuram disulfide,
Phenylethylthiuram disulfide.

More than one of the cure accelerators may be
5 utilized to optimize the desired blend of cured proper-
ties, and processing characteristics. This may also be
desirable to accommodate their solubility limitations of
each individual type of accelerator in EPDM or butyl
rubber. Also the tendency of certain materials to bloom
10 to the surface of the rubber part can be minimized by
maintaining each material at a level well below the
solubility limit in the base rubber elastomer.

To that end, a preferred embodiment of the invention
utilizes a fourth component - a dithiocarbamate type
15 accelerator, such as salts of dialkyldithiocarbamates,
wherein the alkyl groups may have from 1 to 6 carbon
atoms and the salts may be formed with bismuth, cadmium,
copper, iron, lead, potassium, selenium, sodium,
tellerium or zinc. Specific examples are:

20 Zinc dibutyl-dithiocarbamate,
Zinc pentamethylene-dithiocarbamate, Bismuth
dimethyl-dithiocarbamate, Nickel
dibutyl-dithiocarbamate, Copper
dimethyl-dithiocarbamate, Selenium
25 diethyl-dithiocarbamate, Lead
dimethyl-dithiocarbamate, Selenium
dimethyl-dithiocarbamate, Tellurium
dimethyl-dithiocarbamate,

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Tellurium diethyl-dithiocarbamate, Cadmium
diethyl-dithiocarbamate, Zinc
dibenzyl-dithiocarbamate, Zinc
diethyl-dithiocarbamate.

5 In one preferred embodiment EPDM is used as the
elastomer in the composition of this invention. The EPDM
used is a terpolymer of ethylene, one or more olefin
monomer(s) having the general formula $H_2C=CHR$, where R is
an alkyl group having from 1 to 7 carbon atoms. In a
10 preferred embodiment this olefin is propylene. The EPDM
also includes a non-conjugated diene which may be a
 C_6-C_{12} linear or C_9-C_{10} bridged ring hydrocarbon diene
copolymerizable with the aforementioned monomers. The
most commonly employed non-conjugated dienes in the
15 terpolymer of this invention are 1,4-hexadiene,
dicyclopentadiene and 5-ethylidene-2-norbornene.

 In another preferred embodiment the elastomer of the
composition of this invention is butyl rubber. The butyl
rubber of this invention is isobutylene-conjugated diene
20 copolymer comprising from 0.5 to 10% by weight of
conjugated diene. Among the dienes within the
contemplation of this invention are 2-methyl-1,
3-butadiene; 1,3-butadiene; and 2,3-dimethyl-
butadiene-1,3. Of these 2-methyl-1,3-- butadiene is most
25 preferred.

 In yet another preferred embodiment the elastomer is
a mixture of EPDM and butyl rubber, where the EPDM and
butyl rubber has the meanings given in the above two

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paragraphs. There is no limitation on the relative amounts of the two constituents.

The relative ratios of the alkylthiourea to sulfur to thiazole or thiuram may vary widely. Generally a ratio
5 range of 1.0:0.5 to 1:5:5, preferably 1:1:1 to 1:3:3, most preferably 1:1.5:1 to 1:2:2. The dithiocarbamate is preferably added at amounts approximately equal to the thiazole/thiuram component. If a thiazole and a thiuram are added the total amount is represented in the ratios
10 above. It is within the contemplation of this invention that additional ingredients may be incorporated into the composition of this invention. Among the additives that can be present in this composition are processing oils, plasticizers and filler and reinforcing agents. Among
15 the filler and reinforcing agents especially useful in the composition of this invention are carbon black, other silicates, talc, clay, calcium carbonate and the like.

Other ingredients such as activators (zinc oxide, stearic acid, zinc stearate), antidegradants, tackifiers,
20 processing aids may all be considered to be a part of the thermosetting roofing composition of this invention if added. The term curable elastomer will always be presumed to contain a metal oxide such as zinc oxide normally with a fatty acid such as stearic acid or
25 alternatively, with a metal stearate such as zinc stearate which combines the activating effects of the metal oxide and fatty acid.

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The compounding of the composition of this invention may be accomplished by any suitable means including an internal mixer, a transfer mixer, and extruder or an open mill. Independent of the method of compounding the composition, the resulting composition has a cure rate
5 which correlates with the development of cross-linking.

EXAMPLES

The following examples are intended to further illustrate the invention and are not intended to limit
10 the scope of the invention in any manner.

Examples 1-3 and Comparative Experiment A

A master batch(1) concentrate was prepared by adding 60 parts by weight of EPDM to a type "B" laboratory Banbury[™] internal mixer set a 77 revolutions per
15 minute. To this was added 65 parts by weight of carbon black (type N-650); 65 parts by weight of carbon black (type N-339); 65 parts by weight of extender oil (paraffinic petroleum oil, ASTM D2226 Type 104 B, Sunpar[™]2280, R.E. Carroll, Inc.); 30 parts by weight of
20 plasticizer (polybutenes, Indopol[™]H300, Amoco Chemicals Corporation); 10 parts by weight of processing aid (polymer of mixed olefins, Betaprene[™]H-100, Reichhold Chemicals Inc.); 5 parts by weight of zinc oxide and 1 part by weight of stearic acid. To this was added 40
25 parts by weight of EPDM. Thus, the total EPDM constituent comprised 100 parts by weight of the composition. After the remaining EPDM was added, the ram was lowered. Mixing for one minute followed at which

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time the temperature reached 115°C. The ram was then raised, the ram and throat of the mixer were swept, and the ram was again lowered. Mixing continued for an additional 90 seconds at which time the compound

5 temperature reached 138°C. The mixer was stopped, the ram was raised, and the master batch was dropped on a mill to cool.

Four compositions were prepared employing the above master batch. The EPDM uncured rubber, comprising 100

10 parts of the 336 parts by weight of master batch(1), included a blend of 60 parts of a terpolymer noted as "EPDM I." EPDM I is a terpolymer containing 51.9% ethylene, 39.1% propylene and 9.0% 5-ethylidene-2--norbornene, all percentages being by weight. EPDM I had

15 a Mooney viscosity (ML-1 plus 4) at 125°C of 68. The remaining 40 parts by weight of EPDM was a terpolymer denoted as "EPDM II." EPDM II is a terpolymer containing 71.6% ethylene, 23.9% propylene and 4.5% 5-ethylidene--2-norbornene, said percentages based on the total weight

20 of the terpolymer. EPDM II had a Mooney Viscosity (ML-1 plus 4) at 125°C of 77.

To master batch (1), on a mill, was added a constant amount of mercaptobenzothiazole (MBT), zinc 0,0--dibutylphosphorodithioate (ZDBP), zinc dimethyl-

25 dithiocarbamate (ZMDC) and sulfur, the concentrations of which are summarized in Table I below.

Four samples, Samples A and Nos. 1-3, were prepared from these four compositions, whose preparation is

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described above. Each sample, as stated above, included 336 parts by weight of the master batch, comprising 100 parts by weight of EPDM, the exact constituency of which is recited above.

5 To the four samples were added 0.6 parts by weight of dipentaethylenethiuram hexasulfide (DPTH), tetramethylthiuram disulfide (TMTD), 4-morpholinyl-2--benzothioazole disulfide (MBS) and ethylene thiourea (ETU), respectively.

10 These samples were then banded on the back roll of a 20.32 x 40.64 cm mill at a preset temperature of 95°C (front roll) and 65°C (back roll). The nip between the rolls was adjusted to provide a 2.03 mm sheet, while maintaining about 2 cm rolling bank of compound. After
15 30 seconds, air free sheet was cut from the mill and dusted with mica for easier handling.

For testing purposes, six 7.62 x 15.24 cm samples were cut from the dusted sheet and hung in an air circulating oven. From both the unaged and aged samples
20 Standard Dumbbell Die A were cut according to ASTM D-412. Tensile strength at break, measured in mega Pascals, and elongation at break, measured in percent, measurements were made using an Instron[™] tester Model LTD, and the measured results were calculated in
25 accordance with ASTM D-412. All testing was carried out at 23°C.

In addition to strength testing, the curing characteristics of the samples were investigated using a

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Monsanto Rheometer[™], model MPV, at 3° arc, 15 Hz, square die. The curing characteristics are reported as the increase in torque, measured in Centi-Newton meters, between the minimum value and the value obtained after 60 minutes at 100°C.

The results of these tests, as shown in Table I, show the cure efficiency of ethylene-thiourea as the primary accelerator.

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TABLE I

5 Constituents,
 in parts by weight

Example or Comparative Experiment		<u>A</u>	<u>1</u>	<u>2</u>	<u>3</u>
10	Master Batch (1)	336	336	336	336
	MBT	0.6	0.6	0.6	0.6
	ZDBP	1.5	1.5	1.5	1.5
	ZMDC	0.6	0.6	0.6	0.6
15	Sulfur	1.5	1.5	1.5	1.5
	DPTH	0.6	-	-	-
	TMTD	-	0.6	-	-
	MBS	-	-	0.6	-
	ETU	-	-	-	0.6
20	<u>Physical Properties</u>				
	<u>Rheometer 100°C</u>				
	Torque (60), cN.m	73.4	18.1	52.0	125.4
	<u>Unaged</u>				
25	100% modulus, MPa	0.7	0.6	0.6	0.6
	Tensile, MPa	1.9	1.7	1.7	1.7
	Elongation, %	850	860	860	830
	<u>Aged*</u>				
	100% Modulus, MPa	1.4	0.9	1.1	1.6
30	Change, %	(+100)	(+50)	(+85)	(+165)
	Tensile, MPa	10.2	3.9	5.9	11.0
	Change, %	(+435)	(+130)	(+245)	(+545)
35	Elongation, %	700	660	750	640
	Change, %	(-18)	(-23)	(-13)	(-23)

* 7 days at 70°C in a circulating air oven.

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Examples 4-5 and Comparative Experiment B

An additional master batch (2) concentrate was prepared in accordance with the procedure enumerated in Example 1. However, blends of different EPDM's were employed. That is, the relative weight ratios of ethylene and propylene were the same as in Example 1, but lower molecular weight polymers were used. The uncured rubber, comprising 100 parts of the 336 parts by weight of master batch(2), included a blend of 50 parts of a terpolymer noted as "EPDM III" having a Mooney Viscosity (ML-1 plus 4) at 125°C of 55. The remaining 50 parts by weight of EPDM denoted as "EPDM IV" had a Mooney Viscosity (ML-1 plus 4) at 125°C of 50.

Four compositions, denoted as Samples B and Nos. 4-5 were prepared from master batch(2) in which the concentration of MBT, ZDBP, ZMDC and sulfur, were maintained at a constant level of 0.6, 1.5, 0.6 and 1.5 parts, respectively, by weight per 100 parts EPDM. These samples included additional accelerators within the contemplation of this invention. The concentration of these accelerators was maintained constant in all the compositions of this example.

Table II below summarizes and defines the four compositions produced. In addition, these samples were tested in accordance with the procedures set forth in Example 1.

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TABLE II

Constituents,
5 in parts by weight

Example or Comparative Experiment		<u>B</u>	<u>4</u>	<u>5</u>
10	Master Batch (2)	336	336	336
	MBT	0.6	0.6	-
	ZDBP	1.5	1.5	1.5
	ZMDC	0.6	0.6	0.6
	Sulfur	1.5	1.5	1.5
15	DPTH	0.6	-	-
	DETU	-	0.6	0.6

Physical Properties

20	<u>Rheometer 100°C</u>			
	Torque (60), cN.m	58.8	106.2	115.3
	<u>Unaged</u>			
	100% modulus, MPa	0.38	0.41	-
	Tensile, MPa	0.41	0.44	0.41
25	Elongation, %	1000+	1000+	1000+
	<u>Aged*</u>			
	100 Modulus, MPa	0.97	1.66	-
	Change, %	(+155)	(+305)	-
30	Tensile, MPa	4.62.	8.69	9.72
	Change, %	(+1026)	(+1875)	(+2270)
	Elongation, %	650	570	560

35 * 7 days at 70°C in a circulating air oven.

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Examples 6-8

Additional samples No. 6-8 were prepared using the same EPDM sheeting compounds as in Example 1 with the exception of the accelerators used. Along with ETU as a primary accelerator, the following secondary accelerators showed increasing cure rates in the following order: MBS, (1) ZMDC, (2) Tellurium diethyldithiocarbamate (TeEDC), and (3) TMTD. ZMDC, TeEDC and TMTD, all in blends with ETU, exhibit cure rates useful for ambient curing EPDM compounds.

A summary of the constituents of these compositions, Nos. 6-8 and the results of physical testing, as described in Example 1, employing these three samples, are tabulated in Table III.

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TABLE III

<u>Example</u>		<u>6</u>	<u>7</u>	<u>8</u>
5	Master Batch(1)	336	336	336
	Sulfur	1.5	1.5	1.5
	ETU	1.0	1.0	1.0
10	ZMDC	1.0	-	-
	TMTD	-	1.0	-
	Te EDC	-	-	1.0
<u>Physical Properties</u>				
<u>Rheometer 100°C</u>				
15	Torque (60), cN.m	37.3	68.3	44.1
	<u>Unaged</u>			
	100% modulus, MPa ¹	0.6	0.6	0.6
20	Tensile, MPa	1.2	1.2	1.2
	Elongation, %	850	850	850
(1) Masterbatch, not including sulfur or accelerator				
<u>Aged*</u>				
25	100 Modulus, MPa	1.0	1.7	1.3
	Change, %	+67	+183	+117
	Tensile, MPa	3.2	9.3	6.8
30	Change, %	+167	+675	+467
	Elongation, %	480	650	670

* 7 days at 70°C in a circulating air oven.

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Examples 9-20 and Comparative Experiments C-J

Roof sheeting samples were prepared using the same EPDM Master Batch as in Example 1 to further evaluate thioureas versus DPTH in low temperature flashing cure systems. Table IV summarizes the composition of the roof sheeting samples of these examples, as well as the percent improvement in cure rate of the thioureas versus that of DPTH as measured by the increase in torque using a Monsanto Rheometer[™] as described in Example 1.

From the results of these tests it can be seen that even under mild aging conditions, 70°C, that a composition within the contemplation of this invention surprisingly develops a state of cure superior to compositions having DPTH as the primary accelerator. All comparative examples (C-J) would be the prior art compounds disclosed in related U.S. Patents 4,461,875; 4,514,442 and 4,666,785 based on DPTH as a necessary critical component of an ambient cure roofing composition.

5

TABLE IV

10 Constituents, parts by weight

Example or Comparative Experiment	C	9	D	10	E	11	12	13	F	14	15	16	G	17	H	18	I	19	J	20
15 Master Batch(1)	336	336	336	336	336	336	336	336	336	336	336	336	336	336	336	336	336	336	336	336
DPH	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.6
ETU	-	1	-	-	-	1	1	-	-	-	1	-	-	-	-	-	-	-	-	0.6
20 DETU	-	-	-	-	-	-	-	1	-	-	-	1	-	-	-	-	-	-	-	-
DBTU	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.6
NBT	1	1	1	1	1	1	1	1	-	-	-	-	-	-	-	-	-	-	-	0.6
ZMDC	1	1	-	-	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.5
TMTD	-	-	1	1	1	1	1	-	1	1	1	1	1	1	1	1	1	1	1	-
25 ZDBP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
TeEDC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sulfur	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50

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Physical
Properties

Torque (60), cN.m	85.9	90.4	83.6	91.5	56.5	63.3	63.3	56.5	55.4	89.3	78.0	72.3	64.4	140.1	59.9	87.0	45.2	71.2	73.5	117.5
Improvement, %	-	5.2	-	9.4	-	12.0	12.0	0	-	61.2	40.8	30.5	-	117.5	-	45.2	-	57.5	-	59.9

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Examples 21-23 and Comparative Experiment K

Additional roof sheeting samples were prepared using the same EPDM Master Batch (1) as in Example I to show that even at the lower 0.5 part sulfur level, ETU still shows up better than the DPT

. Higher sulfur levels (1.0 and 1.5) further increase the torque change at low temperatures, as expected.

These results appear below in Table V.

TABLE V

10 Constituents,
in parts by weight

Example or Comparative Experiment	<u>K</u>	<u>21</u>	<u>22</u>	<u>23</u>
15 Master Batch (1)	336	336	336	336
DPTH 1.0	-	-	-	-
ETU(1)	-	1.0	1.0	1.0
TMTD 1.0	1.0	1.0	1.0	1.0
20 Sulfur	0.5	0.5	1.0	1.5

Physical PropertiesRheometer 100°C

25 Torque (60)2, cN.m	19.2	23.7	54.2	67.8
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1 1.33 parts of END-75 (75% ETU/25% EPR).

2 Increase in torque between minimum and 60 minute values.

CLAIMS

1. A roofing composition comprising:
- (a) 100 parts of an elastomer selected from the group consisting of ethylene-propylene-non-conjugated diene terpolymer, butyl rubber and mixtures thereof;
- (b) 0.1 to 3.0 parts of a dialkylthiourea;
- (c) 0.4 to 5.0 parts of sulfur;
- (d) 0.4 to 5.0 parts of one or more accelerators selected from the group consisting of thiazoles, thiurams, and dithiocarbamates, all parts by weight and components (b), (c) and (d) are parts per one hundred parts by weight of (a) said composition being essentially free of hexasulfide compounds of the structural formula $[(CH_2)_n NCS]_2S$.
2. A roofing composition in accordance with claim 1 wherein said component (d) comprises a first accelerator selected from the group consisting of thiazoles and thiurams and a second dialkyl dithiocarbamate accelerator.
3. A roofing composition in accordance with claim 2 wherein said first accelerator is tetramethylthiuram disulfide.
4. A roofing composition in accordance with claim 2 wherein said first accelerator is mercaptobenzothiazole.
5. A roofing composition in accordance with claim 2 wherein said second accelerator is a zinc salt of dimethyldithiocarbamate.

6. A roofing composition in accordance with claim 2 wherein said second accelerator is tellurium diethyldithio carbamate.

7. A roofing composition in accordance with claim 1 wherein said sulfur is between 1.0 and 2.0 parts.

8. A roofing composition in accordance with claim 1 wherein said dialkylthiourea is diethylthiourea.

9. A roofing composition in accordance with claim 1 further comprising less than 40 parts of a highly unsaturated thermosetting rubber having an iodine number above 100.

10. A roofing composition in accordance with claim 1 wherein said elastomer is ethylene-propylene-non-conjugated diene terpolymer.

11. A roofing composition in accordance with claim 1 further comprising at least one processing oil.

12. A roofing composition in accordance with claim 1, further comprising at least one plasticizer.

13. A roofing composition in accordance with claim 1, further comprising at least one filler and reinforcing agent.

14. A roofing composition in accordance with claim 13 wherein said filler and reinforcing agent are selected from the group consisting of carbon black, silicates, talc, clay, calcium carbonate, and mixtures thereof.

15. A method of curing a thermosetting rubber composition on a roof in ambient temperature conditions comprising:

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5 (a) blending 100 parts of an elastomer selected from the group consisting of ethylene-propylene-nonconjugated diene terpolymer, butyl rubber and mixtures with and a curative system essentially free of hexasulfide compounds of the structural formula $[(CH_2)_m NCS]_2S$ composed of: 0.1 to 3.0 parts of a dialkylthiourea; 0.4 to 5.0 parts of sulfur; 0.4 to 5.0 parts of one or more accelerators selected from the group consisting of thiazoles, thiruams, and dithiocarbamates, all parts by weight per one hundred parts by weight of said elastomer to form a curable composition; and

10 (b) exposing said curable composition on said roof to air heated above 70°C for a time sufficient to cure said curable composition.

15 16. A method of waterproofing a roof exposed to ambient air comprising the steps of

20 (a) applying cured rubber sheets to a majority of the roof;

(b) overlapping the cured rubber sheets with sheets of an uncured thermosetting rubber roofing composition having an EPDM or butyl rubber elastomer base and a curative system essentially free of hexasulfide compounds of the structural formula $[(CH_2)_n NCS]_2S$ intimately mixed

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therein of 0.1 to 3.0 parts of a dialkyl-thiourea;

0.4 to 5.0 parts of sulfur; 0.4 to 5.0 parts of one or more accelerators selected from the group consisting of thiazoles, thirams, and dithiocarbamates, all parts by weight per one hundred parts by weight of elastomer base; and

(c) curing said thermosetting rubber roofing composition by exposure to said ambient conditions.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US 90/04473**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 08 L 23/16, C 08 L 23/22, C 08 K 5/39

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System

Classification Symbols

IPC⁵

C 08 L, C 08 K

Documentation Searched other than Minimum Documentation
to the extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ¹⁰ Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² Relevant to Claim No. ¹³

X	DE, B, 1298267 (FARBENFABRIKEN BAYER) 26 June 1969 see column 1, line 1 - column 2, line 11 --	1-15
A	DE, A, 2058951 (VAKUUM VULK HOLDINGS) 8 June 1972 see claim 1 --	1
A	FR, A, 1463232 (CELANESE CORPORATION OF AMERICA) 23 December 1966 see abstract ----	1

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IV. CERTIFICATION

Date of the Actual Completion of the International Search
28th November 1990

Date of Mailing of this International Search Report
19. 12. 90

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

M. Peis

M. PEIS

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9004473

SA 39476

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-B- 1298267		FR-A- 1455518 GB-A- 1130547	
DE-A- 2058951	08-06-72	None	
FR-A- 1463232		BE-A- 673557 CH-A- 1707265 DE-A- 1543251 GB-A- 1134889 NL-A- 6516132	10-06-66 12-06-69 13-06-66

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